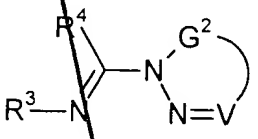
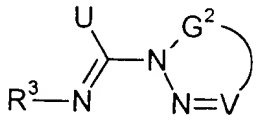
Claims

We claim:

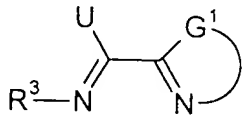
1. A batch or continuous process for the polymerization of olefins, comprising contacting one or more monomers selected from compounds of the formula $RCH=CHR^1$ with a Group 8-10 transition metal complex of a ligand of the formula **VI**, **XII**, **IX**, **XIII**, **XIV**, **XV**, or **XXII** and optionally a Bronsted or Lewis acid,



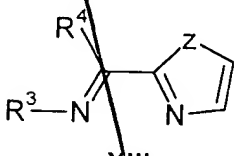
VI



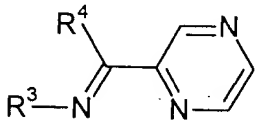
XII



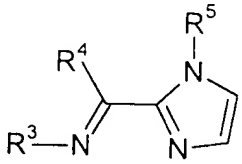
IX



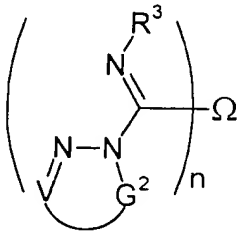
XIII



XIV



XV



XXII

wherein R and R^1 are independently H, hydrocarbyl, fluoroalkyl, or R and R^1 may be linked to form a cyclic olefin;

R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is H, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^5 is hydrocarbyl or substituted hydrocarbyl;

Z is O or S;

U is $-OR^{10}$, $-SR^{10}$, $-SeR^{10}$ or $-NR^{10}R^8$, wherein R^{10} and R^8 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, or silyl, and in addition R^{10} and R^8 may collectively form a ring with nitrogen;

G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1, C, and N;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2, V, N, and N;

V is $-CR^6$, N, or $-PR^6R^9$; wherein, R^6 and R^9 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

Ω is hydrocarbyl or substituted hydrocarbyl; and,

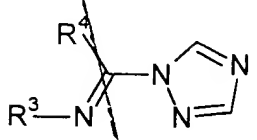
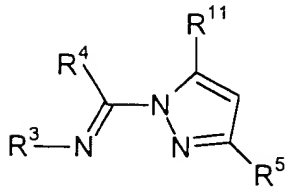
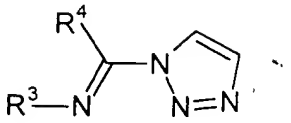
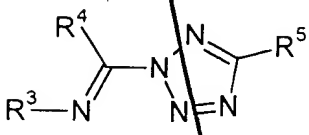
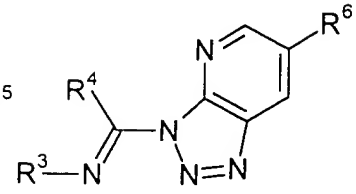
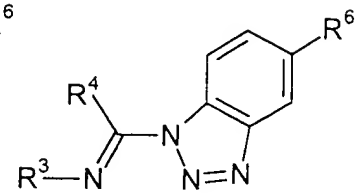
n is an integer between 2 and 6.

2. The process of claim 1 wherein the monomer of the formula $RCH=CHR^1$ is selected from ethylene, propylene, 1-butene, 1-hexene, and 1-octene.

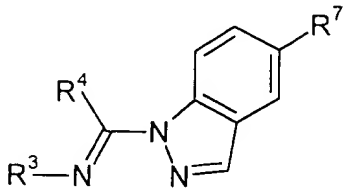
3. The process of claim 1 wherein the group 8-10 transition metal is nickel.

4. The process of claim 3 wherein a Lewis acid is used, and said Lewis acid is methylaluminoxane.

5. The process of claim 4 wherein the ligand of formula **VI** is selected from:

and



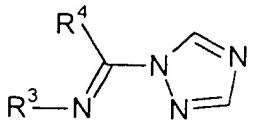
wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is H, hydrocarbyl, substituted hydrocarbyl, or silyl;

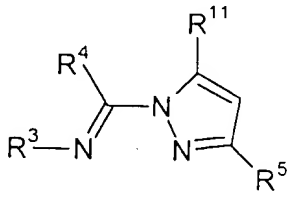
R^5, R^6 and R^{11} are independently H, hydrocarbyl, or substituted hydrocarbyl;

R^7 is H, hydrocarbyl, substituted hydrocarbyl, or NO_2.

6. The process of claim 5 wherein the ligand of formula **VI** is selected from:

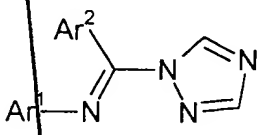
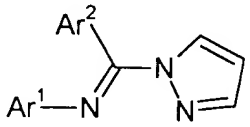


and



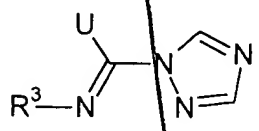
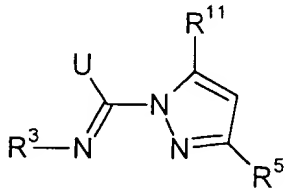
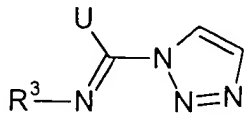
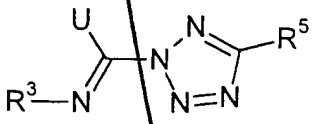
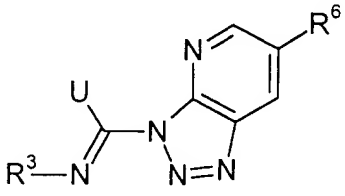
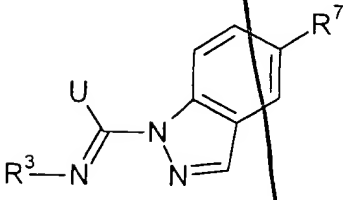
wherein R^3 is hydrocarbyl or substituted hydrocarbyl;
R^4 is H, hydrocarbyl, substituted hydrocarbyl, or silyl; and,
R^5 and R^{11} are independently H, hydrocarbyl, or substituted hydrocarbyl.

7. The process of claim 6 wherein the ligand of formula **VI** is


or


wherein Ar^1 is 2,6-dimethylphenyl or 2,6-diisopropylphenyl; and,
Ar^2 is phenyl or 1-naphthyl.

8. The process of claim 4 wherein the ligand of formula **XII** is selected from: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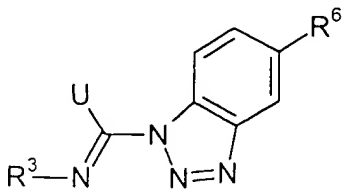


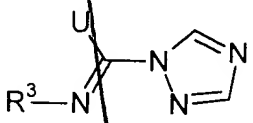
wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

U is $-OR^{10}$, $-SR^{10}$, $-SeR^{10}$ or $-NR^{10}R^8$, wherein R^{10} and R^8 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, or silyl, and in addition R^{10} and R^8 may collectively form a ring with nitrogen;

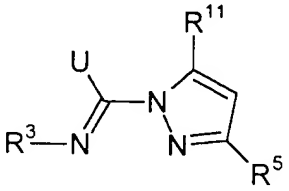
R^5, R^6 and R^{11} are independently H, hydrocarbyl, or substituted hydrocarbyl;

R^7 is H, hydrocarbyl, substituted hydrocarbyl, or $-NO_2$.

9. The process of claim 8 wherein the ligand of formula **XII** is selected from:



and

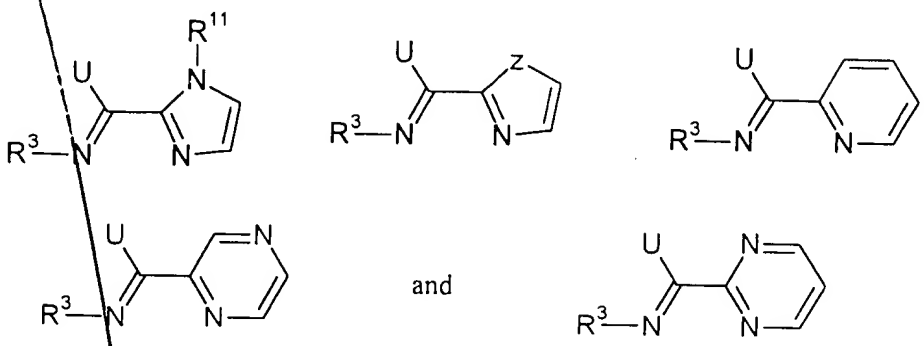


wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

U is $-OR^{10}$, $-SR^{10}$, $-SeR^{10}$ or $-NR^{10}R^8$, wherein R^{10} and R^8 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, or silyl, and in addition R^{10} and R^8 may collectively form a ring with nitrogen;

R^5 and R^{11} are independently H, hydrocarbyl, or substituted hydrocarbyl.

10. The process of claim 4 wherein the ligand of formula **IX** is selected from:



and

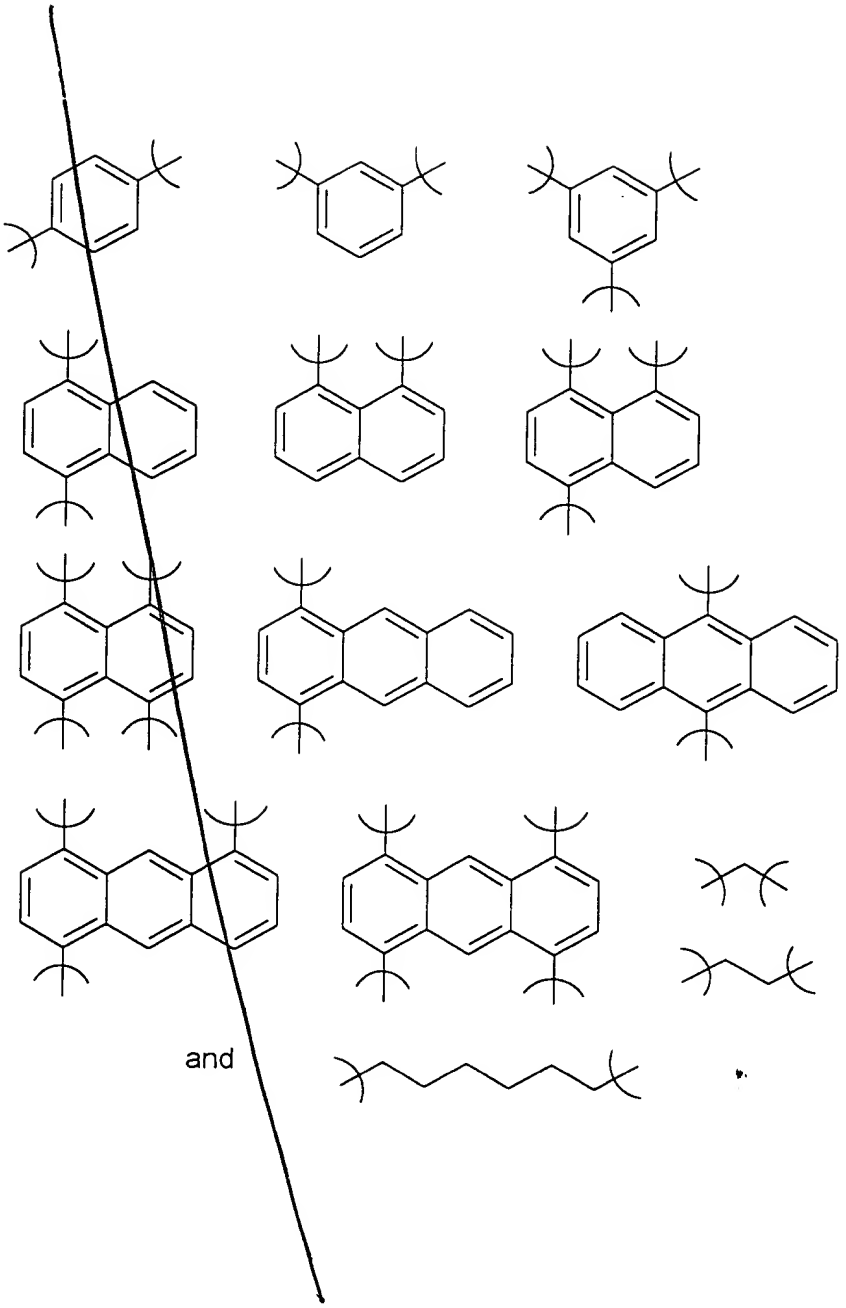
wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

R^{11} is hydrocarbyl, or substituted hydrocarbyl;

U is $-OR^{10}$, $-SR^{10}$, $-SeR^{10}$ or $-NR^{10}R^8$, wherein R^{10} and R^8 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, or silyl, and in addition R^{10} and R^8 may collectively form a ring with nitrogen; and

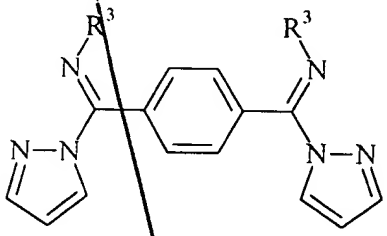
Z is oxygen or sulfur.

11. The process of claim 4 wherein the ligand is of formula **XXII** and Ω is selected from

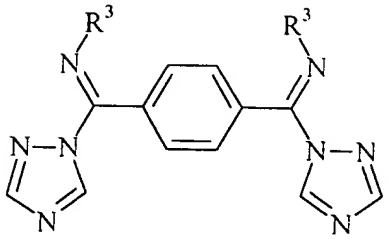


and

12. The process of claim 11 wherein the ligand of formula **XXII** is selected from



and



wherein, R^3 is 2,6-disubstituted phenyl.

13. A process for the polymerization of olefins comprising contacting one or more monomers of the formula $RCH=CHR^1$ with a binucleating or multinucleating ligand complexed to a Group 8-10 transition metal M and one or more Lewis acids, wherein the Lewis acid or acids are bound to one or more heteroatoms which are π-conjugated to the donor atom or atoms bound to the transition metal M; and R and R^1 are each, independently selected from hydrogen, hydrocarbyl, fluoroalkyl, or may be linked to form a cyclic olefin.

14. The process of Claim 13 wherein the transition metal M is nickel.

15. The process of Claim 14 wherein the Lewis acid is a boron or aluminum containing Lewis acid.

16. The process of claim 4 wherein the polymerization is conducted in an inert solvent.

17. The process of claim 5, 8, 10 or 11 wherein the polymerization is conducted in an inert solvent.

18. The process of claim 4 wherein the transition metal olefin polymerization catalyst system is attached to a solid support.

19. The process of claim 5, 8, 10, or 11 wherein the transition metal olefin polymerization catalyst system is attached to a solid support.

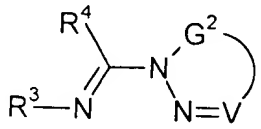
20. The process of claim 18 wherein the polymerization is conducted in an inert solvent.

21. The process of claim 19 wherein the polymerization is conducted in an inert solvent.

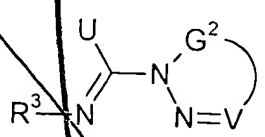
22. The process of claim 18 wherein the polymerization is conducted in the gas phase.

23. The process of claim 19 wherein the polymerization is conducted in the gas phase.

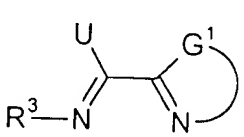
24. An olefin polymerization catalyst comprising (a) a Group 8-10 transition metal, (b) a ligand of the formula **VI**, **XII**, **IX**, **XIII**, **XIV**, **XV**, or **XXII** and optionally (c) a Bronsted or Lewis acid,



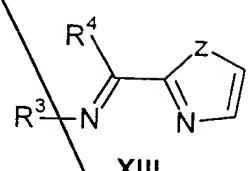
VI



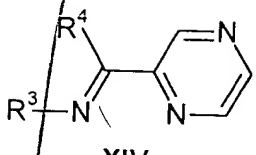
XII



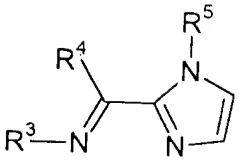
IX



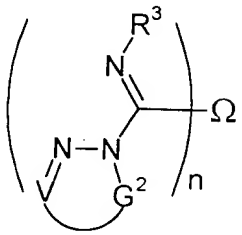
XIII



XIV



XV



XXII

wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is H, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^5 is hydrocarbyl or substituted hydrocarbyl;

Z is O or S;

U is $-OR^{10}$, $-SR^{10}$, $-SeR^{10}$ or $-NR^{10}R^8$, wherein R^{10} and R^8 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, or silyl, and in addition R^{10} and R^8 may collectively form a ring with nitrogen;

G^1 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^1, C, and N;

G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2, V, N, and N;

V is $-CR^6$, N, or $-PR^6R^9$; wherein, R^6 and R^9 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus;

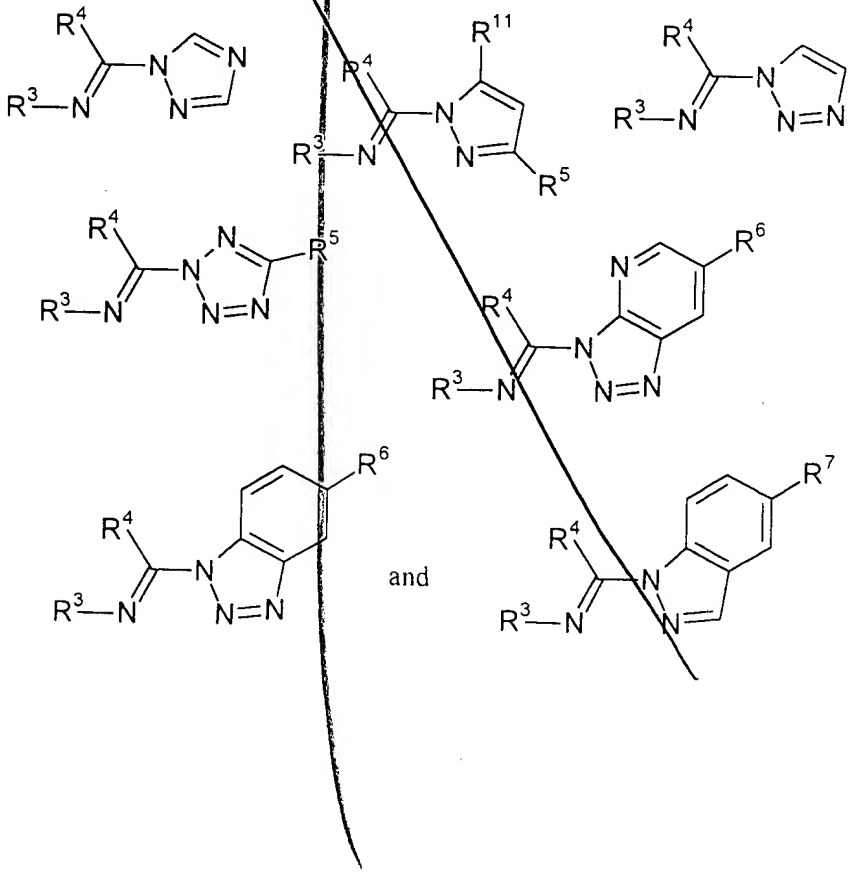
Ω is hydrocarbyl or substituted hydrocarbyl; and,

n is an integer between 2 and 6.

25. The catalyst of claim 24 wherein the Group 8-10 transition metal is Ni.

26. The catalyst of claim 25 wherein a Lewis acid is used, and said Lewis acid is methylaluminoxane.

27. The catalyst of claim 26 wherein the ligand of formula VI is selected from:



and

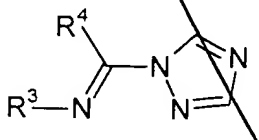
wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is H, hydrocarbyl, substituted hydrocarbyl, or silyl;

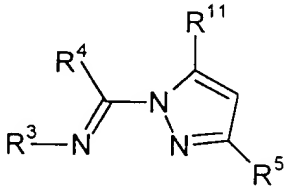
R^5, R^6 and R^{11} are independently H, hydrocarbyl, or substituted hydrocarbyl;

R^7 is H, hydrocarbyl, substituted hydrocarbyl, or NO_2.

28. The catalyst of claim 27 wherein the ligand of formula **VI** is selected from:



and

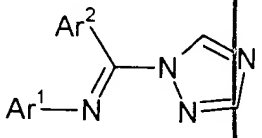


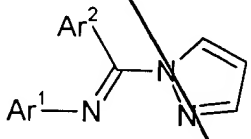
wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is H, hydrocarbyl, substituted hydrocarbyl, or silyl; and,

R^5 and R^{11} are independently H, hydrocarbyl, or substituted hydrocarbyl.

29. The catalyst of claim 28 wherein the ligand of formula **VI** is

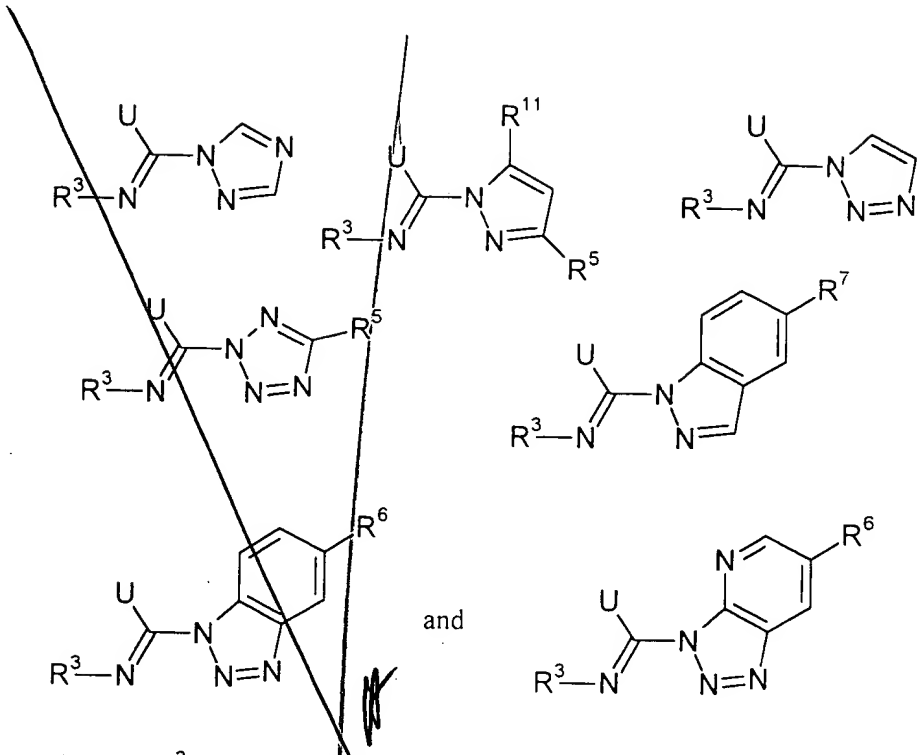




wherein Ar^1 is 2,6-dimethylphenyl or 2,6-diisopropylphenyl; and,

Ar^2 is phenyl or 1-naphthyl.

30. The catalyst of claim 26 wherein the ligand of formula **XII** is selected from:



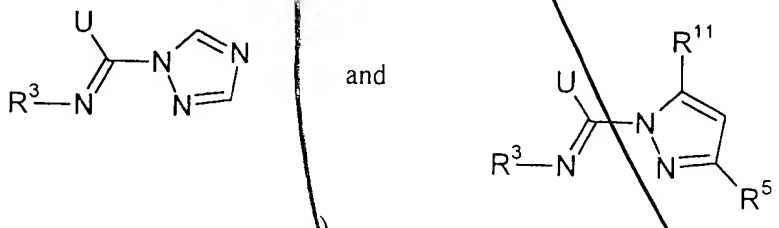
wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

U is $-OR^{10}$, $-SR^{10}$, $-SeR^{10}$ or $-NR^{10}R^8$, wherein R^{10} and R^8 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, or silyl, and in addition R^{10} and R^8 may collectively form a ring with nitrogen;

R^5, R^6 and R^{11} are independently H, hydrocarbyl, or substituted hydrocarbyl;

R^7 is H, hydrocarbyl, substituted hydrocarbyl, or $-NO_2$.

31. The catalyst of claim 30 wherein the ligand of formula **XII** is selected from:

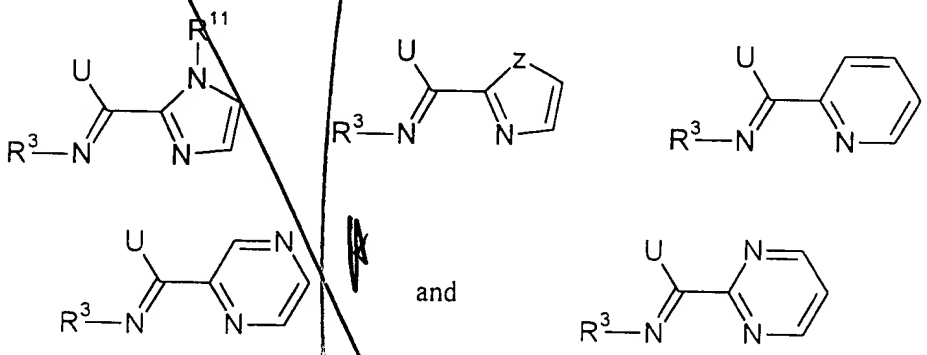


wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

U is $-OR^{10}$, $-SR^{10}$, $-SeR^{10}$ or $-NR^{10}R^8$, wherein R^{10} and R^8 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, or silyl, and in addition R^{10} and R^8 may collectively form a ring with nitrogen;

R^5 and R^{11} are independently H, hydrocarbyl, or substituted hydrocarbyl.

32. The catalyst of claim 26 wherein the ligand of formula **IX** is selected from:



and

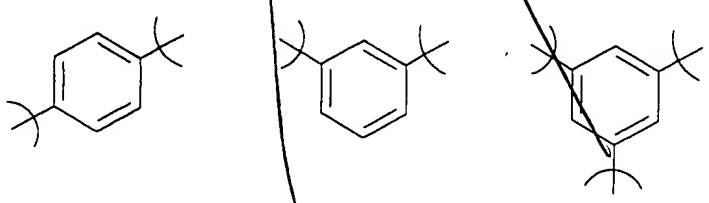
wherein R^3 is hydrocarbyl or substituted hydrocarbyl;

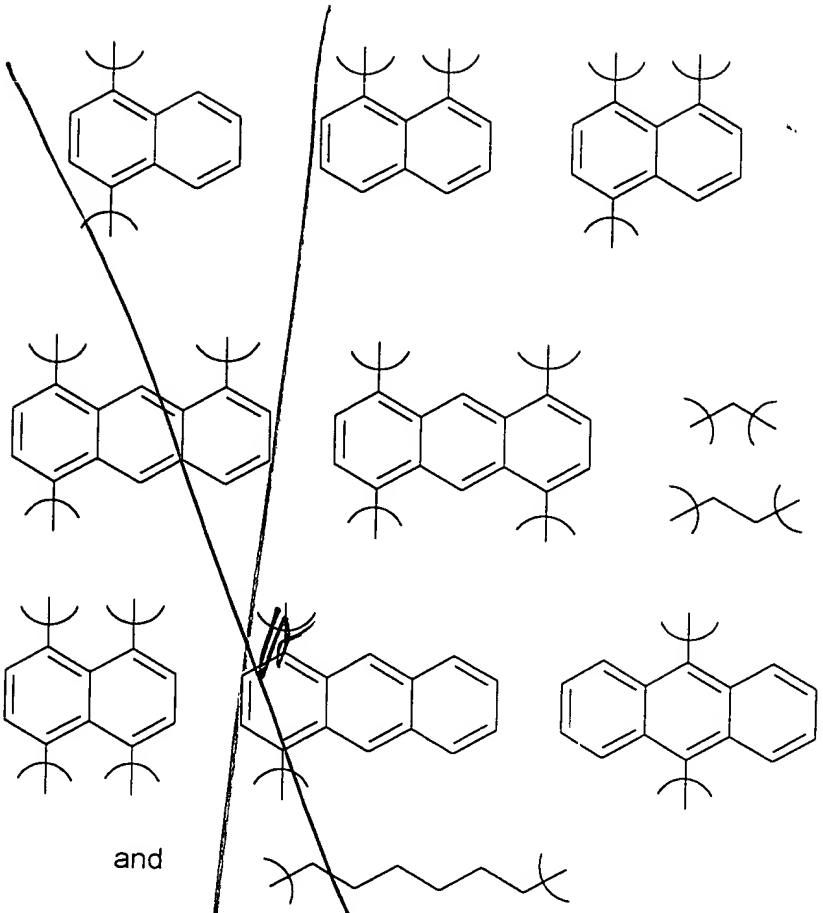
R^{11} is hydrocarbyl or substituted hydrocarbyl;

U is $-OR^{10}$, $-SR^{10}$, $-SeR^{10}$ or $-NR^{10}R^8$, wherein R^{10} and R^8 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, or silyl, and in addition R^{10} and R^8 may collectively form a ring with nitrogen; and

Z is oxygen or sulfur.

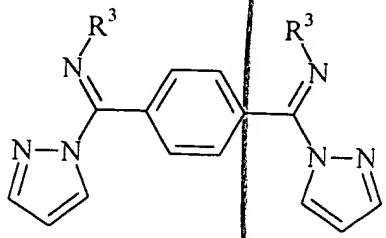
33. The catalyst of claim 26 wherein the ligand is of formula **XXII** and Ω is selected from:



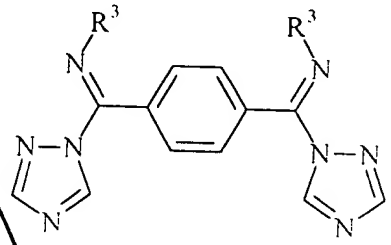


and

34. The catalyst of claim 33 wherein the ligand of formula **XXII** is selected from:

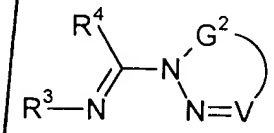


and



wherein, R^3 is 2,6-disubstituted phenyl.

35. A composition comprising (a) a group 8-10 transition metal M, (b) one or more Lewis acids, and (c) a binucleating or multinucleating ligand of the formula VI



VI

wherein the Lewis acid or acids are bound to one or more heteroatoms which are π-conjugated to the donor atoms bound to the transition metal M;

R^3 is hydrocarbyl or substituted hydrocarbyl;

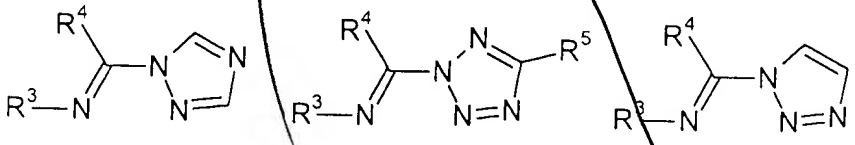
R^4 is H, hydrocarbyl, substituted hydrocarbyl, or silyl;

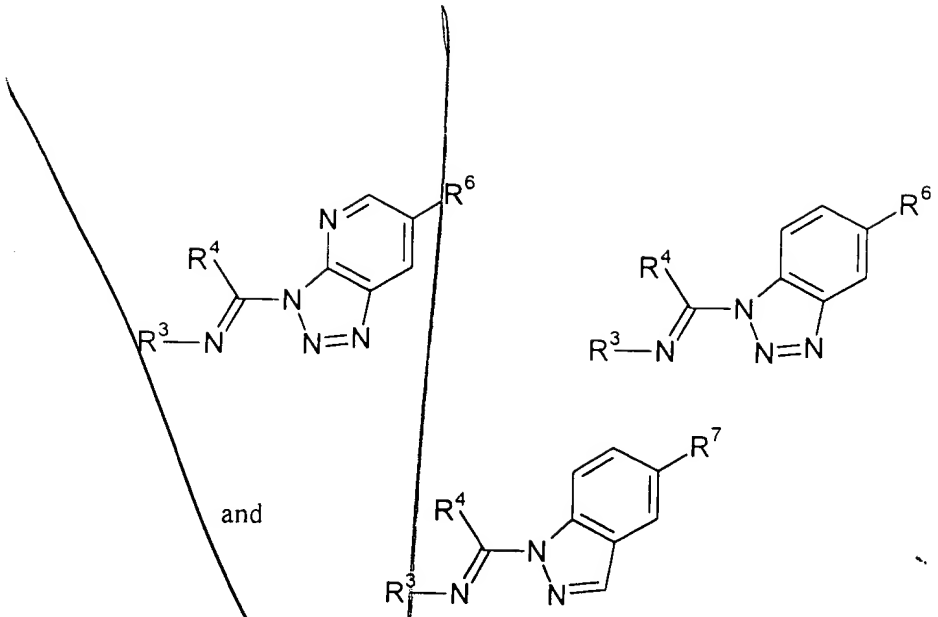
G^2 is hydrocarbyl or substituted hydrocarbyl and may comprise a carbocyclic or heterocyclic ring, thereby forming a 5-membered or 6-membered heterocyclic ring comprising G^2, V, N and N;

V is $-CR^6$, N, or $-PR^6R^9$; wherein, R^6 and R^9 are each independently selected from H, hydrocarbyl, substituted hydrocarbyl, silyl or heteroatom connected hydrocarbyl, and in addition, R^6 and R^9 may collectively form a ring with phosphorus.

36. The composition of claim 35 wherein the transition metal M is Ni(II), and the Lewis acid is a boron or aluminum containing acid.

37. The composition of claim 36 wherein the compound of formula VI is selected from:





and

wherein the Lewis acid or acids are bound to one or more heteroatoms which are π-conjugated to the donor atom or atoms bound to the transition metal M;

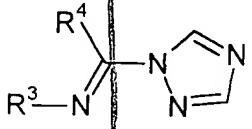
R^3 is hydrocarbyl or substituted hydrocarbyl;

R^4 is H, hydrocarbyl, substituted hydrocarbyl, or silyl;

R^5 and R^6 are independently H, hydrocarbyl, or substituted hydrocarbyl;

R^7 is H, hydrocarbyl, substituted hydrocarbyl, or $-NO_2$.

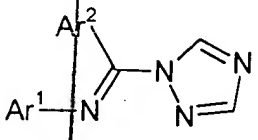
38. The composition of claim 37 wherein the ligand of formula VI is



wherein R^3 is hydrocarbyl or substituted hydrocarbyl; and,

R^4 is H, hydrocarbyl, substituted hydrocarbyl, or silyl.

39. The composition of claim 38 wherein the ligand of formula VI is



wherein Ar^1 is 2,6-dimethylphenyl or 2,6-diisopropylphenyl; and, Ar^2 is phenyl or 1-naphthyl.

40. The catalyst of claim 24 wherein the catalyst is attached to a solid support.

41. The catalyst of claim 27 wherein the catalyst is attached to a solid support.

42. The catalyst of claim 30 wherein the catalyst is attached to a solid support.

43. The catalyst of claim 32 wherein the catalyst is attached to a solid support.

44. The catalyst of claim 33 wherein the catalyst is attached to a solid support.